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4-Sulfamoylanilinium perchlorate

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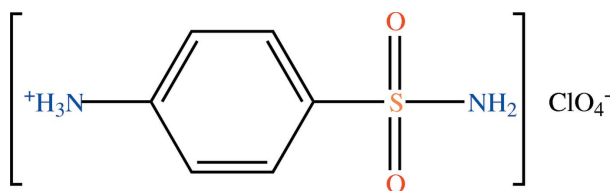
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.022; wR factor = 0.061; data-to-parameter ratio = 14.3.

In the crystal of the title salt, $\text{C}_6\text{H}_9\text{N}_2\text{O}_2\text{S}^+\cdot\text{ClO}_4^-$, the components are linked by $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds, forming a three-dimensional network. The cations are connected along a and b axes, leading to linear and zigzag $C(3)$ and $C(8)$ chain motifs, respectively. A cation–anion interaction along the c axis leads to a $C_2^2(12)$ chain motif. $R_3^3(18)$ and $R_3^3(20)$ ring motifs are observed as cation–anion-type interactions. These hydrogen-bonding ring and chain motifs are localized at $z = 0$ or 1, leading to alternate hydrophilic and hydrophobic regions along the c axis as a result of the stacking of anions and the aromatic cationic parts.

Related literature

For the first use of sulfanilamide, see: Buttle *et al.* (1936). For related structures, see: Ravikumar *et al.* (2013); Pandiarajan *et al.* (2011); Topacli & Kesimli (2001). For graph-set motifs, see Etter *et al.* (1990).



Experimental

Crystal data

$\text{C}_6\text{H}_9\text{N}_2\text{O}_2\text{S}^+\cdot\text{ClO}_4^-$
 $M_r = 272.66$
Monoclinic, $P2_1$

$a = 4.9158$ (10) Å
 $b = 10.514$ (2) Å
 $c = 9.814$ (2) Å

$\beta = 93.716$ (3)°
 $V = 506.15$ (18) Å³
 $Z = 2$
Mo $K\alpha$ radiation

$\mu = 0.60$ mm⁻¹
 $T = 293$ K
 $0.24 \times 0.16 \times 0.12$ mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
5796 measured reflections

2367 independent reflections
2361 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.023$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.022$
 $wR(F^2) = 0.061$
 $S = 1.08$
2367 reflections
166 parameters
5 restraints

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.31$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.26$ e Å⁻³
Absolute structure: Flack (1983), 1287 Friedel pairs
Flack parameter: 0.00 (4)

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N1}-\text{H1A}\cdots\text{O1}^{\text{i}}$	0.88 (1)	2.12 (1)	2.953 (2)	160 (3)
$\text{N1}-\text{H1B}\cdots\text{O6}^{\text{ii}}$	0.88 (3)	2.30 (3)	3.086 (2)	149 (2)
$\text{N2}-\text{H2A}\cdots\text{O5}^{\text{i}}$	0.88 (1)	2.19 (1)	3.044 (2)	164 (3)
$\text{N2}-\text{H2B}\cdots\text{O2}^{\text{iii}}$	0.88 (1)	2.16 (2)	2.876 (2)	139 (2)
$\text{N2}-\text{H2C}\cdots\text{O4}^{\text{iv}}$	0.88 (1)	2.30 (2)	2.858 (2)	122 (2)
$\text{N2}-\text{H2C}\cdots\text{O5}$	0.88 (1)	2.37 (2)	3.058 (2)	136 (2)

Symmetry codes: (i) $x + 1, y, z$; (ii) $-x + 1, y + \frac{1}{2}, -z + 1$; (iii) $-x + 2, y + \frac{1}{2}, -z + 1$; (iv) $-x + 1, y + \frac{1}{2}, -z$.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL/PC*; molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXTL/PC*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NG5332).

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supplementary materials

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4-Sulfamoylanilinium perchlorate

R. Anitha, S. Athimoolam, M. Gunasekaran and B. Sridhar

Comment

Sulfa drugs, mostly the derivatives of sulfanilamide, have been an integral part of our medical history. They were the first effective chemotherapeutic agents to be widely used for the treatment of bacterial infection in humans and animals (Topacli & Kesimli, 2001). The uses of Sulfanilamide, was started during 1936 (Buttle *et al.*, 1936) and the grandparent of the sulfonamide family of drugs that are still in use today. The nitrate and sulfate complexes of sulfanilamide (Pandiarajan *et al.*, 2011; Ravikumar *et al.*, 2013) were already reported. In continuation of our interest on the sulfanilamide complexes, the synthesis of the title compound and its title structure, bis(4-sulfamoylanilinium) sulfate, is described here. In the title structure, a protonated sulfomylanilinium cation and a perchlorate anion constitute the asymmetric part (Fig. 1). The protonation on the one of N sites is confirmed from C—N bond distance. The geometrical parameters of the cation are in agreement with the reported sulfomylanilinium structures in 4-sulfomylanilinium nitrate (Pandiarajan *et al.*, 2011) and Bis(4-sulfomylanilinium) sulfate (Ravikumar *et al.*, 2013).

The crystal structure is stabilized through intricate three dimensional hydrogen bonding network formed through N—H \cdots O interactions (Table 1; Fig. 2). All the hydrogen atoms attached to both the nitrogen atoms of the cation is involved in the hydrogen bonding interactions as donors. All the oxygen atoms in the cation and anion, except the O3 atom present in the anion, are acting as acceptor atoms and involved in the hydrogen bonding interactions. One of the N—H \cdots O hydrogen bonds is observed to be bifurcated hydrogen bond, with one donor hydrogen (Table 1): N2—H3N \cdots O4 ($-x + 1, y + 1/2, -z$) and N2—H3N \cdots O5. Among the hydrogen bonds, two are cation-cation type and other four hydrogen bonds are cation-anion type. In the cation-cation type, N1—H2N \cdots O1($1 + x, y, z$) is making a chain C(3) motif extending along *a*-axis of the unit cell. Another N2—H5N \cdots O2($2 - x, 1/2 + y, 1 - z$) hydrogen bond is connecting the cations along *b*-axis of the unit cell through zigzag chain C(8) motifs. Thus cations are connected directly only along *a* & *b*-axes. Whereas along *c*-axis the interactions are cation-anion type, *i.e.*, the cations and anions are connected through N1—H1N \cdots O6($-x + 1, y + 1/2, -z + 1$) and N2—H3N \cdots O4($-x + 1, y + 1/2, -z$) hydrogen bonds leading to chain C₂2'(12) motif.

Further, cations and anions are connected through N1—H2N \cdots O1($1 + x, y, z$), N2—H3N \cdots O5 and N2—H4N \cdots O5($1 + x, y, z$) leading to a ring R₃³(18) motifs. Another ring R₃³(20) motif is formed through N1—H1N \cdots O6($-x + 1, y + 1/2, -z + 1$), N2—H4N \cdots O5($1 + x, y, z$) and N2—H5N \cdots O2($-x + 2, y + 1/2, -z + 1$) hydrogen bonds. These ring R₃³(20) motifs are arranged adjacently and making a chain C₃³(10) motif extending along *b*-axis of the unit cell. These hydrogen bonding ring and chain motifs are localized at *z* = 0 or *z* = 1 leading to alternate hydrophilic and hydrophobic regions along *c* axis as a result of the stacking of anions and the aromatic cationic parts.

Experimental

The synthesis of the title compound was carried out by heating of the mixture of sulphanilamide (1.7 g) and perchloric acid (0.5 ml of 98%) in water with the stoichiometric ratio of 1:1 (at 60°C) under reflux for 1 h. Colourless needle type crystals of the title compound suitable for single-crystal X-ray analysis with the approximate size of 1.8 cm times 0.6 cm

times 0.4 cm were obtained by slow evaporation at room temperature. The measured sample was cut from a bigger crystal. Caution: Although no problems were encountered in this work, perchlorate compounds are potentially explosive. They should be prepared in small amounts and handled with care.

Refinement

All the H atoms except the atoms involved in hydrogen bonds were positioned geometrically and refined using a riding model, with $C-H = 0.93 \text{ \AA}$ and $U_{iso}(H) = 1.2 U_{eq}(\text{parent atom})$. H atoms involved in hydrogen bonds were located from differential fourier map and refined isotropically with the distance restraint (*DFIX*) for appropriate distance ($0.88(1) \text{ \AA}$). From the measured 5796 total reflections, 1287 are Friedel opposites.

Computing details

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT* (Bruker, 2001); program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL/PC* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXTL/PC* (Sheldrick, 2008).

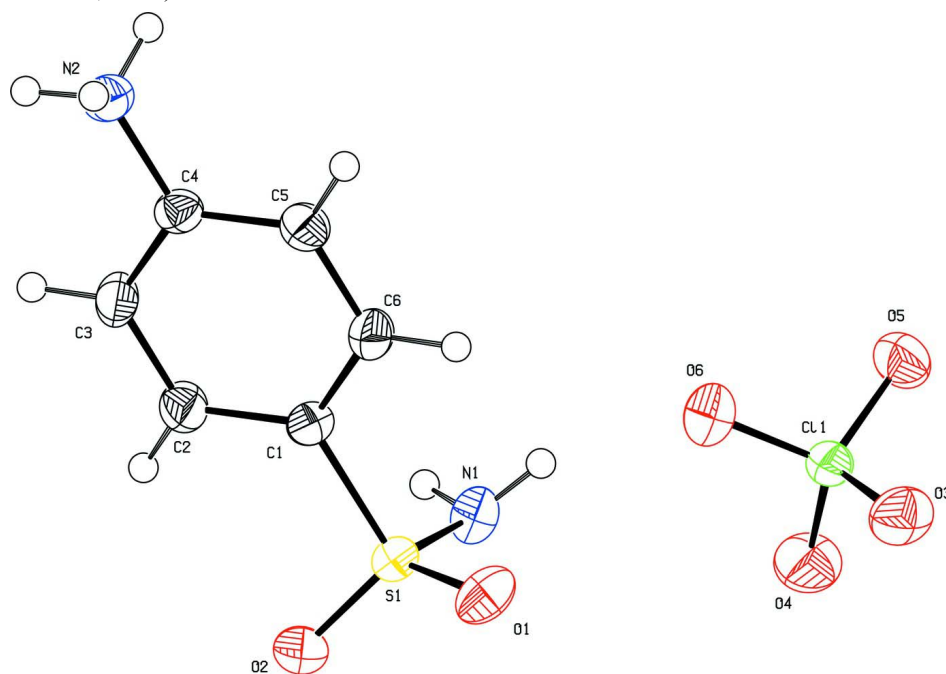


Figure 1

The title molecule with the atom numbering scheme. The displacement ellipsoids are shown at the 50% probability level.

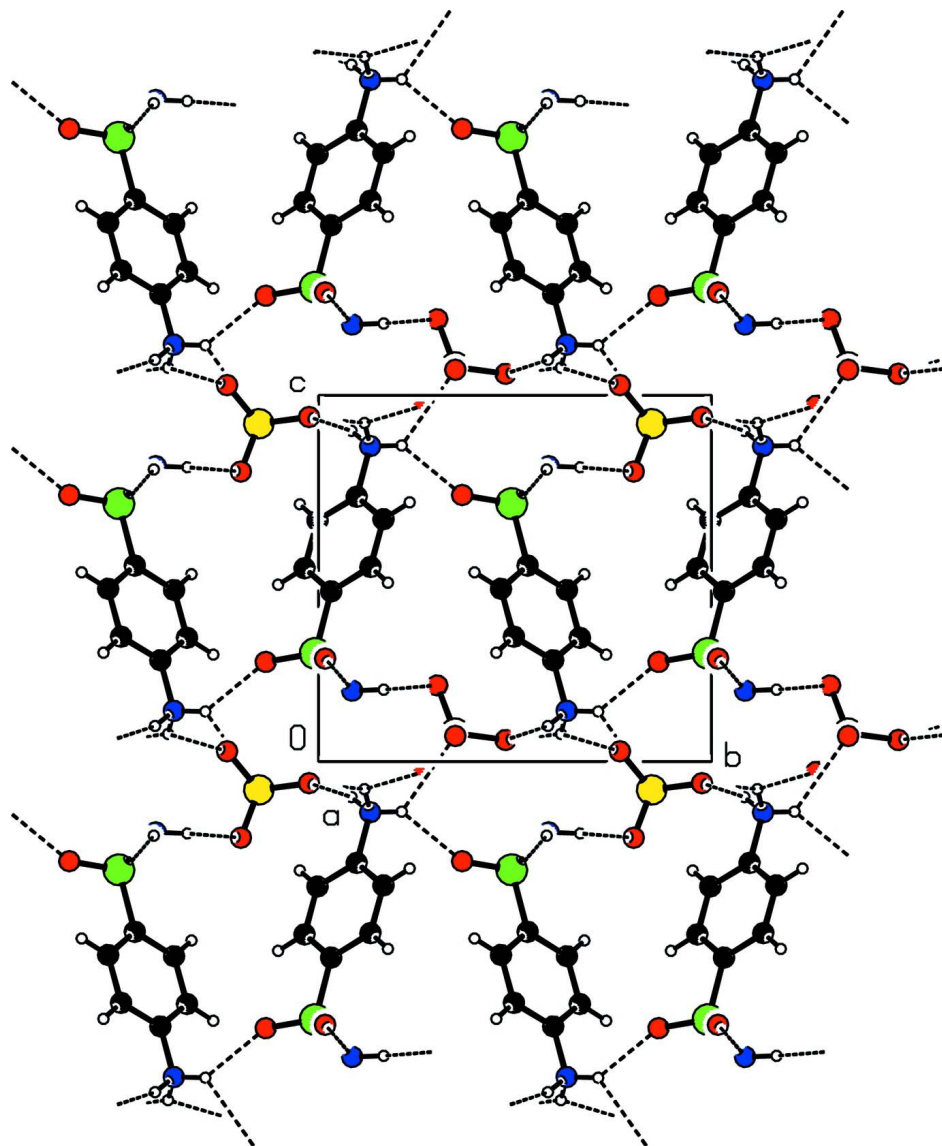


Figure 2

Packing diagram of the title compound viewed down the *a*-axis. The H-bonds are shown as dashed lines.

4-Sulfomylanilinium perchlorate

Crystal data

$\text{C}_6\text{H}_9\text{N}_2\text{O}_2\text{S}^+\cdot\text{ClO}_4^-$

$M_r = 272.66$

Monoclinic, $P2_1$

Hall symbol: $P\ 2_1y$

$a = 4.9158(10)\ \text{\AA}$

$b = 10.514(2)\ \text{\AA}$

$c = 9.814(2)\ \text{\AA}$

$\beta = 93.716(3)^\circ$

$V = 506.15(18)\ \text{\AA}^3$

$Z = 2$

$F(000) = 280$

$D_x = 1.789\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 2412 reflections

$\theta = 2.5\text{--}24.7^\circ$

$\mu = 0.60\ \text{mm}^{-1}$

$T = 293\ \text{K}$

Needle, colourless

$0.24 \times 0.16 \times 0.12\ \text{mm}$

Data collection

Bruker SMART APEX CCD area-detector
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

ω scans

5796 measured reflections

2367 independent reflections

2361 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.023$

$\theta_{\text{max}} = 28.0^\circ$, $\theta_{\text{min}} = 2.1^\circ$

$h = -6 \rightarrow 6$

$k = -13 \rightarrow 13$

$l = -12 \rightarrow 12$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.022$

$wR(F^2) = 0.061$

$S = 1.08$

2367 reflections

166 parameters

5 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: inferred from
neighbouring sites

H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0315P)^2 + 0.1129P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.001$

$\Delta\rho_{\text{max}} = 0.31 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.26 \text{ e } \text{\AA}^{-3}$

Extinction correction: *SHELXTL/PC* (Sheldrick,
2008), $F_c^* = kF_c[1 + 0.001 \times F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.189 (7)

Absolute structure: Flack (1983), 1287 Friedel
pairs

Flack parameter: 0.00 (4)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) etc. and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.8057 (3)	0.53210 (15)	0.53535 (15)	0.0244 (3)
C2	1.0030 (3)	0.46394 (16)	0.47189 (16)	0.0295 (3)
H2	1.0919	0.3964	0.5169	0.035*
C3	1.0672 (3)	0.49695 (19)	0.34095 (16)	0.0293 (3)
H3	1.1998	0.4523	0.2973	0.035*
C4	0.9310 (3)	0.59698 (15)	0.27676 (15)	0.0235 (3)
C5	0.7316 (3)	0.66524 (16)	0.33789 (17)	0.0281 (3)
H5	0.6419	0.7320	0.2920	0.034*
C6	0.6676 (3)	0.63237 (17)	0.46891 (17)	0.0294 (3)
H6	0.5338	0.6768	0.5119	0.035*
N1	0.9084 (3)	0.58560 (16)	0.80644 (15)	0.0315 (3)
N2	0.9994 (3)	0.63135 (15)	0.13833 (15)	0.0279 (3)
O1	0.4527 (2)	0.51671 (14)	0.71892 (14)	0.0380 (3)
O2	0.8370 (3)	0.36510 (13)	0.72799 (14)	0.0385 (3)

H1A	1.0834 (17)	0.578 (3)	0.797 (3)	0.070 (9)*
H1B	0.847 (5)	0.665 (3)	0.803 (3)	0.047 (7)*
H2A	1.120 (4)	0.584 (2)	0.100 (3)	0.055 (7)*
H2B	1.052 (5)	0.7108 (9)	0.134 (3)	0.053 (8)*
H2C	0.863 (4)	0.617 (3)	0.078 (2)	0.048 (7)*
Cl1	0.58672 (7)	0.34769 (3)	0.07752 (4)	0.02621 (11)
O3	0.8773 (2)	0.34793 (17)	0.06980 (15)	0.0409 (3)
O4	0.4686 (3)	0.26701 (16)	−0.02835 (16)	0.0477 (4)
O5	0.4874 (3)	0.47611 (13)	0.05900 (15)	0.0399 (3)
O6	0.5169 (3)	0.30181 (14)	0.20823 (15)	0.0445 (3)
S1	0.73500 (7)	0.49156 (3)	0.70441 (4)	0.02528 (11)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0265 (7)	0.0256 (7)	0.0217 (7)	−0.0006 (6)	0.0055 (5)	0.0017 (5)
C2	0.0328 (7)	0.0291 (8)	0.0268 (7)	0.0085 (6)	0.0034 (6)	0.0022 (6)
C3	0.0318 (7)	0.0310 (8)	0.0258 (7)	0.0071 (7)	0.0066 (5)	−0.0021 (6)
C4	0.0246 (6)	0.0244 (7)	0.0217 (6)	−0.0033 (5)	0.0026 (5)	0.0002 (5)
C5	0.0295 (8)	0.0260 (8)	0.0289 (7)	0.0051 (6)	0.0039 (6)	0.0046 (6)
C6	0.0286 (7)	0.0294 (8)	0.0311 (8)	0.0067 (6)	0.0091 (6)	0.0020 (7)
N1	0.0303 (7)	0.0361 (8)	0.0285 (7)	0.0003 (6)	0.0048 (6)	−0.0044 (6)
N2	0.0309 (7)	0.0293 (7)	0.0239 (6)	−0.0016 (6)	0.0045 (5)	0.0020 (6)
O1	0.0264 (6)	0.0523 (9)	0.0362 (6)	−0.0018 (5)	0.0090 (5)	0.0027 (6)
O2	0.0532 (8)	0.0281 (7)	0.0355 (6)	0.0052 (6)	0.0131 (5)	0.0080 (5)
Cl1	0.02693 (18)	0.02327 (17)	0.02901 (19)	−0.00278 (13)	0.00626 (12)	−0.00363 (14)
O3	0.0255 (6)	0.0483 (7)	0.0495 (7)	0.0003 (6)	0.0069 (5)	−0.0073 (7)
O4	0.0489 (8)	0.0478 (8)	0.0466 (9)	−0.0168 (7)	0.0033 (7)	−0.0193 (7)
O5	0.0413 (7)	0.0271 (7)	0.0522 (8)	0.0048 (6)	0.0092 (6)	0.0027 (6)
O6	0.0560 (8)	0.0424 (8)	0.0366 (7)	−0.0042 (6)	0.0155 (6)	0.0060 (6)
S1	0.02663 (18)	0.02599 (19)	0.02388 (17)	0.00010 (14)	0.00668 (12)	0.00191 (14)

Geometric parameters (Å, °)

C1—C2	1.386 (2)	N1—S1	1.6113 (16)
C1—C6	1.393 (2)	N1—H1A	0.875 (5)
C1—S1	1.7692 (15)	N1—H1B	0.88 (3)
C2—C3	1.387 (2)	N2—H2A	0.877 (5)
C2—H2	0.9300	N2—H2B	0.876 (5)
C3—C4	1.377 (2)	N2—H2C	0.876 (5)
C3—H3	0.9300	O1—S1	1.4289 (13)
C4—C5	1.383 (2)	O2—S1	1.4345 (14)
C4—N2	1.466 (2)	Cl1—O6	1.4328 (14)
C5—C6	1.387 (2)	Cl1—O4	1.4345 (14)
C5—H5	0.9300	Cl1—O3	1.4355 (12)
C6—H6	0.9300	Cl1—O5	1.4432 (14)
C2—C1—C6	121.01 (14)	H1A—N1—H1B	115 (3)
C2—C1—S1	118.86 (12)	C4—N2—H2A	117.2 (19)
C6—C1—S1	120.12 (12)	C4—N2—H2B	111.4 (18)

C1—C2—C3	119.67 (15)	H2A—N2—H2B	108 (3)
C1—C2—H2	120.2	C4—N2—H2C	111.9 (18)
C3—C2—H2	120.2	H2A—N2—H2C	97 (3)
C4—C3—C2	118.80 (15)	H2B—N2—H2C	110 (3)
C4—C3—H3	120.6	O6—C11—O4	109.89 (10)
C2—C3—H3	120.6	O6—C11—O3	110.16 (9)
C3—C4—C5	122.36 (15)	O4—C11—O3	108.68 (9)
C3—C4—N2	118.57 (14)	O6—C11—O5	109.20 (9)
C5—C4—N2	119.06 (14)	O4—C11—O5	110.13 (10)
C4—C5—C6	118.85 (14)	O3—C11—O5	108.75 (9)
C4—C5—H5	120.6	O1—S1—O2	119.15 (9)
C6—C5—H5	120.6	O1—S1—N1	107.62 (8)
C5—C6—C1	119.31 (14)	O2—S1—N1	107.65 (9)
C5—C6—H6	120.3	O1—S1—C1	107.46 (7)
C1—C6—H6	120.3	O2—S1—C1	106.66 (7)
S1—N1—H1A	111 (2)	N1—S1—C1	107.86 (8)
S1—N1—H1B	112.7 (17)		
C6—C1—C2—C3	0.9 (3)	C2—C1—C6—C5	−0.8 (2)
S1—C1—C2—C3	−177.99 (13)	S1—C1—C6—C5	178.07 (13)
C1—C2—C3—C4	−0.3 (3)	C2—C1—S1—O1	−147.96 (13)
C2—C3—C4—C5	−0.3 (3)	C6—C1—S1—O1	33.10 (16)
C2—C3—C4—N2	−179.92 (15)	C2—C1—S1—O2	−19.12 (16)
C3—C4—C5—C6	0.4 (2)	C6—C1—S1—O2	161.93 (14)
N2—C4—C5—C6	−179.99 (15)	C2—C1—S1—N1	96.28 (15)
C4—C5—C6—C1	0.2 (2)	C6—C1—S1—N1	−82.67 (15)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N1—H1A \cdots O1 ⁱ	0.88 (1)	2.12 (1)	2.953 (2)	160 (3)
N1—H1B \cdots O6 ⁱⁱ	0.88 (3)	2.30 (3)	3.086 (2)	149 (2)
N2—H2A \cdots O5 ⁱ	0.88 (1)	2.19 (1)	3.044 (2)	164 (3)
N2—H2B \cdots O2 ⁱⁱⁱ	0.88 (1)	2.16 (2)	2.876 (2)	139 (2)
N2—H2C \cdots O4 ^{iv}	0.88 (1)	2.30 (2)	2.858 (2)	122 (2)
N2—H2C \cdots O5	0.88 (1)	2.37 (2)	3.058 (2)	136 (2)

Symmetry codes: (i) $x+1, y, z$; (ii) $-x+1, y+1/2, -z+1$; (iii) $-x+2, y+1/2, -z+1$; (iv) $-x+1, y+1/2, -z$.